SCOPE AND LIMITATION OF RUTHENIUM ION CATALYZED OXIDATION OF COAL AS AN ANALYTICAL TOOL FOR AN ALIPHATIC PORTION OF COAL ORGANIC MATERIALS

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Introduction

We have been investigating a chemical structure of Japanese bituminous Akabira coal by Curie-point pyrolysis GC/MS coupled with CP/MAS ^{13}C NMR and proposed a unit chemical structure of the coal on the basis of these results.[1] In that paper, we had pointed out more precise and quantitative evaluation of chemical bonds connecting aromatic rings should be clarified in order to evaluate more precise chemical structures of coal organic materials (COM). As for this, Stock *et al.*, investigated ruthenium ion catalyzed oxidation (RICO) of coal.[2] Ruthenium tetroxide is well known to have a property to attack selectively sp^2 carbons of organic substrates: for example, in this oxidation arylalkanes and diarylalkanes could be converted to aliphatic monocarboxylic and dicarboxylic acids, respectively. One of the most critical points of this reaction is believed to be the difficulty in attaining quantitative analyses of lower carboxylic acids because they are main products, showing high volatility. Stock *et al.* and Strausz *et al.* had applied the isotope dilution method[2] and esterification with phenacyl bromide[3] for the quantitative analysis, respectively. The former, however, needs preparation of deuterium-labeled carboxylic acids and the later has a slow rate of conversion of the carboxylic acids to their phenacyl esters.

In this paper, we have examined quantitative determination of carboxylic acids resulted from RICO reaction and proposed the method to accomplish this, applying this for RICO reaction of Illinois #6 (American subbituminous), Akabira (Japanese bituminous), and Zao Zhuang (Chinese bituminous) coals.

Experimental Section

Reagents, Samples, and Instruments.

As to Illinois #6 coal, Argonne premium coal sample was used. Whole coals employed in this paper were pulverized under 100 mesh and dried at 100 °C *in vacuo* (5 mmHg) for 10 h prior to use. Solvents were distilled according to conventional methods. Other reagents were commercially available and used without further purification.

Procedure for RICO Reaction of Coal.

RuCl$_3$ (40 mg) and coal (1 g) were add to a 100 ml flask containing MeCN (20 ml), CCl$_4$ (20 ml), and H$_2$O (30 ml), the mixture being stirred magnetically for 1 h. NaIO$_4$ (10 g) was added gradually and the resulting mixture was stirred at 40 °C for 24 h. After the end of the reaction, the mixture was filtered to remove an inorganic residue. The filtrate was analyzed with the following two methods; (i) For analysis of lower carboxylic acids ($\leq$C$_6$), aqueous NaOH solution (5 %, 100 ml) and ether (100 ml) were added to the filtrate and the aqueous phase was separated. This aqueous solution was diluted to 1000 ml by using deionized water and 5 ml portion of this solution was analyzed by a DIONEX 2000i/sp ion chromatograph (HPICE-AS-1 column). (ii) For analysis of higher carboxylic acids (C$_7$$\leq$), diluted hydrochloric acid (5 %, 100 ml) were added to the filtrate and the resulting solution was extracted with 100 ml of ether, twice. The ethereal solution was dried over sodium sulfate. After evaporation of ether, carboxylic acids produced were esterified with diazomethane and analyzed with a Shimadzu GC-8APF (CBP-1 capillary column, ϕ 0.50 mm x 25 m) and a Shimadzu QP-2000A GC-MS (CBP-1 capillary column, ϕ 0.25 mm x 25 m).

Results and Discussion

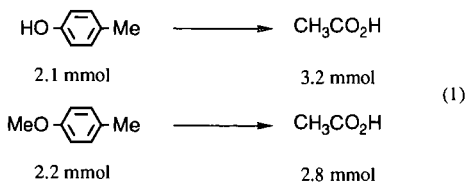### Problems in RICO Reaction of Coal.

At first, we have examined availability of ion chromatography to analyze a mixture of lower carboxylic acids. Figure 1 shows ion chromatograms of a model mixture containing succinic, formic, acetic, propionic, butyric, and valeric acids

and RICO products of Akabira coal, this suggesting that peak separation is relatively good and analysis of these carboxylic acids is not disturbed by the presence of I^- and IO_x^- ions contained in the reaction mixture.

We have discussed the possible factors affecting the results of RICO reaction; (i) evolution of acetic acid from hydrolysis of MeCN, (ii) oxidation rate of COM, and (iii) further decomposition of carboxylic acids produced with $RuCl_3$-$NaIO_4$. As to the first possibility, Strausz *et al.* had pointed out that EtCN should be used in place of MeCN for analysis of methyl groups attached to aromatic moieties.[3] In fact, treatment of mixture of MeCN, CCl_4, and H_2O with $RuCl_3$-$NaIO_4$ at 40 °C for 24 h was found to afford acetic acid along with small amount of formic acid. These results suggest that, in this solvent system, reliable yields of carboxylic acids having more than three carbons (propionic acid or higher) could be obtained, however, yield of acetic acid is unreliable because of contamination of the decomposition product from the solvent system. Subsequently, we decided to employ EtCN instead of MeCN, as Strausz *et al.* pointed out. Treatment of a mixture of EtCN, CCl_4, and H_2O with $RuCl_3$-$NaIO_4$ afforded formic, acetic, propionic, and butyric acids, however, yield of acetic acid from EtCN was less than that from MeCN, this suggesting that EtCN is preferable than MeCN for analysis of acetic acid.

Table 1 summarizes the results of treatment of a mixture of lower carboxylic acids with $RuCl_3$-$NaIO_4$ in the two solvent systems (MeCN or EtCN with CCl_4-H_2O). In the case of MeCN, 1.4 mmol excess of acetic acid was observed along with 0.74 mmol of formic acid. On the other hands, in the case using EtCN, excess amounts of acetic acid observed reduced to 0.77 mmol. On the basis of these results, we employed two tertiary solvent systems; one containing EtCN for analysis of acetic acid from α–methyl groups and another containing MeCN for analysis of carboxylic acids with more than three carbons (propionic acid or higher).

RICO reaction was carried out using coal model compounds in the solvent system containing EtCN. The reaction of p-cresol and p-methylanisole proceeded almost completely, while excess acetic acids (1.1 and 0.6 mmol) were produced. These results suggest that evolution of acetic acid from hydrolysis of EtCN was 0.8 ± 0.2 mmol, this value showing good agreement with the value in Table 1. These results also suggested a reactivity of oxygen containing compounds is relatively high. Since coal usually has these functional groups, it is supposed that the reactivity of coal should be high.

$$HO-\langle\!\!\!\bigcirc\!\!\!\rangle-Me \longrightarrow CH_3CO_2H$$

2.1 mmol   3.2 mmol

$$MeO-\langle\!\!\!\bigcirc\!\!\!\rangle-Me \longrightarrow CH_3CO_2H$$

2.2 mmol   2.8 mmol

(1)

In order to get more precise information about the conversion rate of coal under above reaction conditions, we have carried out the following experiments; after the end of RICO reaction of Akabira coal, the resulting reaction mixture was filtered, the filter cake being washed thoroughly with water and CH_2Cl_2. The residue was found almost completely to be dissolved in water and CH_2Cl_2, this suggesting that the coal was converted to soluble products almost completely.

RICO Reaction of Three Coals.

Illinois #6 (C 76.6 wt%, daf), Akabira (82.3 %), and Zao Zhuang coals (86.6 %) were employed in this study. As described in the former section, the ion chromatograph was used for analysis of lower carboxylic acids ($\leq C_6$) and GC and GC-MS were used for higher carboxylic acids ($C_7\leq$) after esterification with diazomethane. In the case of the analysis of acetic acid produced, EtCN was used as a co-solvent.

Figure 2 shows gas chromatograms for RICO reaction products of Akabira coal, this indicating that Akabira coal has a wide range of alkyl side chains from C_7 to

C_{30}. Figure 3 shows the plot of yield of whole monocarboxylic acids against carbon numbers. From Figure 3, it is clear that yields of carboxylic acids decreased monotonically from acetic acid to valeric acid, this suggesting that methyl group is dominant substituents of aromatic moieties. This is parallel with the findings reported so far. As to yields of lower carboxylic acids, three coals showed very similar distribution of carboxylic acids, indicating aliphatic substitution of aromatic moieties ranging from methyl to hexyl groups are very similar to each other. These results showed a good agreement with the results reported by Stock et al.[2] On the other hands, yields of higher carboxylic acids are different among three coals: a lower rank coal has longer alkyl side chains attached to aromatic moieties than those of higher rank coal.

Since this RICO reaction has some limitations, a precise information about all parts of aliphatic functional groups in COM can be hardly obtained only based on this reaction. However, we have to evaluate this RICO reaction to be able to afford us very useful information about aliphatic portions of COM by the combination use of ^{13}C NMR.

References
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Table 1. Treatment of Free Lower Carboxylic Acid with $RuCl_3$-$NaIO_4$ in RCN-CCl_4-H_2O Mixed Solvent[a]

	MeCN			EtCN		
	Used amount (mmol)	Observed amount (mmol)[b]	Difference (mmol)	Used amount (mmol)	Observed amount (mmol)[b]	Difference (mmol)
Formic acid	-	0.74	+0.74	-	0.083	+0.083
Acetic acid	1.74	3.11	+1.37	0.87	1.64	+0.77
Propionic acid	0.64	0.50	-0.14	0.68	0.92	+0.24
n-Butyric acid	0.49	0.48	-0.01	0.59	1.31	+0.72
n-Valeric acid	0.19	0.16	-0.03	0.50	0.47	-0.03

[a]Treatment of carboxylic acids with $RuCl_3$ (40 mg) and $NaIO_4$ (10 g) were carried out in the solvent system containing RCN (20 ml), CCl_4 (20 ml), and H_2O (30 ml) at 40 °C for 24 h. [b]Determined by an ion chromatograph.
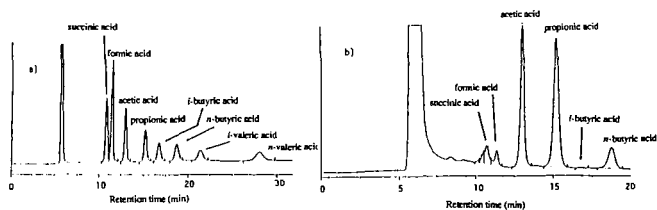
Figure 1. Ion chromatograms of model mixture of lower carboxylic acids (a) and the reaction products from the oxidation of Akabira coal (b)
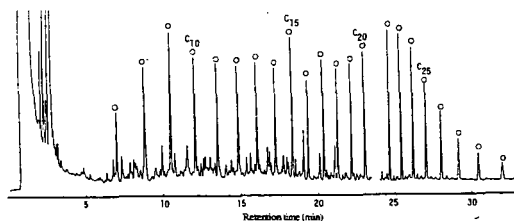

Figure 2. A gas chromatogram for carboxylic acid methyl esters from the oxidation reaction of Akabira coal
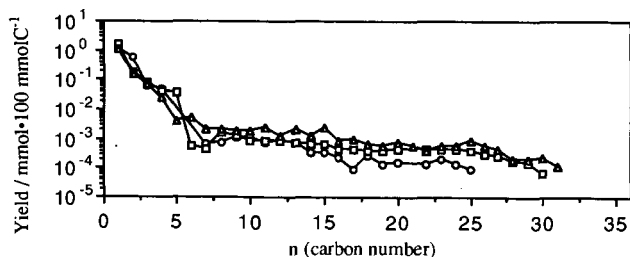

Figure 3. Yields of fatty monoacids, $C_nH_{(2n+1)}CO_2H$, from oxidation of the coals; Illinois No. 6 ($\triangle$), Akabira ($\square$), and Zao Zhuang coals ($\bigcirc$)